Research of Reactive Ion and Plasma-Chemical Etching Effect on Diamond Coating Surface Morphology

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Abstract. The effect of treatment by reactive ion etching in an argon atmosphere, and hydrogen plasma etching in a glow discharge plasma on the surface of the diamond films was investigated. Diamond films were deposited by the Chemical Vapor Deposition method on the hard alloy VK-8 substrates. The crystallites direction under the influence of argon ion beam processing was changed by 45 degrees from the original. The surface morphology becomes more developed (an average value of 20%) by etching in a glow discharge plasma in an atmosphere of hydrogen. Raman spectroscopy, Scanning Electron Microscope and Atomic Force Microscopy were used to determine the phase and microstructure composition of deposited films.

INTRODUCTION

For the last 10 years the investigations in the field of application of diamond coatings are more actively developed. Diamond coatings differ from the others by the presence of a large number of unique parameters required for different application areas, starting from the hardening coatings, optical elements and to the semiconductor electronics [1]. The diamond coatings have high thermal conductivity among all well-known solids (900-2300 W/m·K), they are wear-resistant, chemical and radiation exposure inert, as well as they possess a wide bandwidth of optical radiation from deep ultraviolet to far infrared. Pure diamond is a good electric insulator (specific resistance is $\sim 10^{16}$ Ω·cm at a room temperature). When diamond is doped, its specific resistance can vary in a wide range from 10 to 10^6 (Ω·cm), that converts diamond into wide-band-gap semiconductor with an energy gap width of 5.4 eV that enables to use it under high working powers and in a wide range of temperatures without a significant distortion of the signal passing through devises based on diamond. The thermal expansion coefficient (TEC) of diamond is one of the lowest and is equal to TEC of invar at a room temperature ($0.8 \cdot 10^{-6}$ K^{-1}) [1].

For using the diamond potential, it is necessary to carry out the processes on its treatment. Regarding the columnar structure of growth, as the thickness increases, the morphology of the obtained surface becomes more developed and random that has a negative influence on many indicators, which are significant for the application of diamond films [2]. For the optical diamond systems and membranes being thin self-sustaining structures, the irregularities on the surface have a negative influence on the optical characteristics, generating extra faces for the dispersion and reflection of light. As such coatings are used in manufacture of the machining tool, the developed surface decreases the precision of the cutting edge that restricts the finish and has a negative influence on the wear resistance of the coating. In the field of the diamond electronics, the surface morphology predefines many electrophysical parameters, starting from breakdown voltages and ending with the quality of heat exchange [3].

The treatment of the diamond surface is a complicated and labour intensive process [4]. The most difficulties are caused by the diamond resistance to different physical and chemical effects. Also during the film synthesis, the diamond crystals grow chaotically, therefore the surface is covered with spikes and protrusions of different shapes, sizes, and growth directions.

There are several most used technologies to treat the surface of the diamond films [5]:

i. Polishing by the abrasive materials with the physical destruction and removal of the surface irregularities. This method is the most destructive, difficult to be controlled and it leaves many foreign particles.

Prospects of Fundamental Sciences Development (PFSD-2016)
AIP Conf. Proc. 1772, 040007-1–040007-5; doi: 10.1063/1.4964566
Published by AIP Publishing. 978-0-7354-1430-3/$30.00

ii. Laser ablation of the film surface, which is the action by the laser pulse with a high energy on the surface. The disadvantages of this method are a high energy of a pulse and a low depth resolution, it causes a high heating and eliminating the sample curvature [6].

iii. Charged particle bombardment – destruction of the surface layer by the accelerated particles.

The technology of charged particle bombardment is the most promising, because regardless of the sample curvature it enables to change the morphology of its surface rather effectively and makes the least destructive contribution to the structure of the surface. The reactive ion etching and etching in a glow discharge plasma makes the highest interest for the study. The reactive ion etching is caused by the physical destruction of the surface by the directed accelerated inert particles of argon or nitrogen. It enables to obtain the required etch profile regardless of the composition and structure of the film [7]. Due to the high particle energy, insignificant surface amorphization is possible, as well as the occurrence of intergranular phases, which often contain different modifications of carbonic compounds. Etching in the glow discharge plasma is based on the action of the accelerated particles on the film, with the simultaneous physical and chemical destruction of the surface that is responsible for the fast etching compared to the charged ion bombardment. For the diamond coatings, the most effective gas-etchant is hydrogen, because it binds and removes carbonic groups from the surface without leaving reaction waste products. Here consideration must be given to the destruction which occurs faster in the least stable points, where there is the inner voltage or defects, therefore the etch profile is nonuniform over the surface. The purpose of the conducted study is the analysis of the effect of by reactive ion etching in an argon atmosphere, and hydrogen plasma etching in a glow discharge plasma treatments on the surface of the diamond films.

METHODS AND MATERIALS

In the work, a group of the hard alloy VK-8 (based on WC-Co) samples with the diamond coatings which were deposited with identical parameters in glow discharge plasma that provided minimum dispersion under the initial conditions. Before deposition, the samples were cleaned from impurities by the sequential treatment in an ultrasonic bath YaXun YX-9055 (50 kHz), in acetone - 5 min and after it in ($18 \cdot 10^6$ Ω·cm) deionized water - 3 min.

The deposition method includes the gas activation and coating deposition in glow discharge plasma. Under a pressure in a vacuum chamber of 40 Torr, the 6.5 W charge was generated, it is ignited between two tungsten electrodes fixed in cooled holders. The H_2 and CH_4 gas mixture in the ratio of 9:1 was injected into the reactor through the gas-distributing "shower" system, which is provided the uniform gas flow overall the area of the substrate [8]. The substrate was located under plasma on the water-cooled substrate holder. The time of the coating synthesis was 2 hours under the temperature of the substrate 900±25 C°, the thickness of the obtained coating was 20±1 μm.

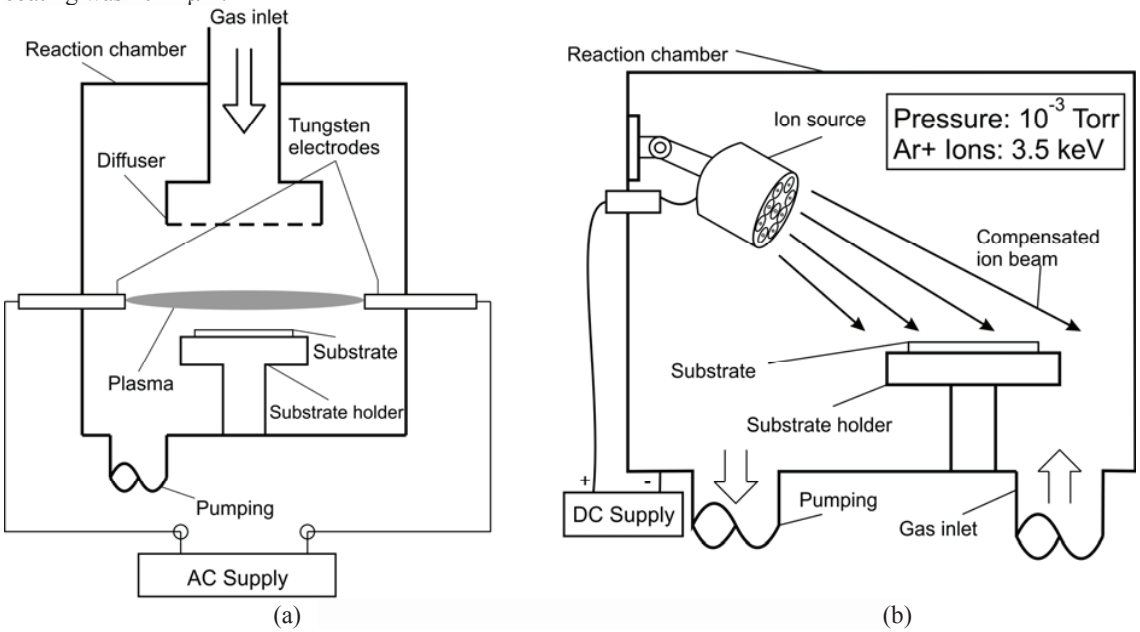


FIGURE 1. Experimental scheme: a) diamond coating deposition in a glow discharge plasma b) diamond ion etching using an ion source with anode layer .

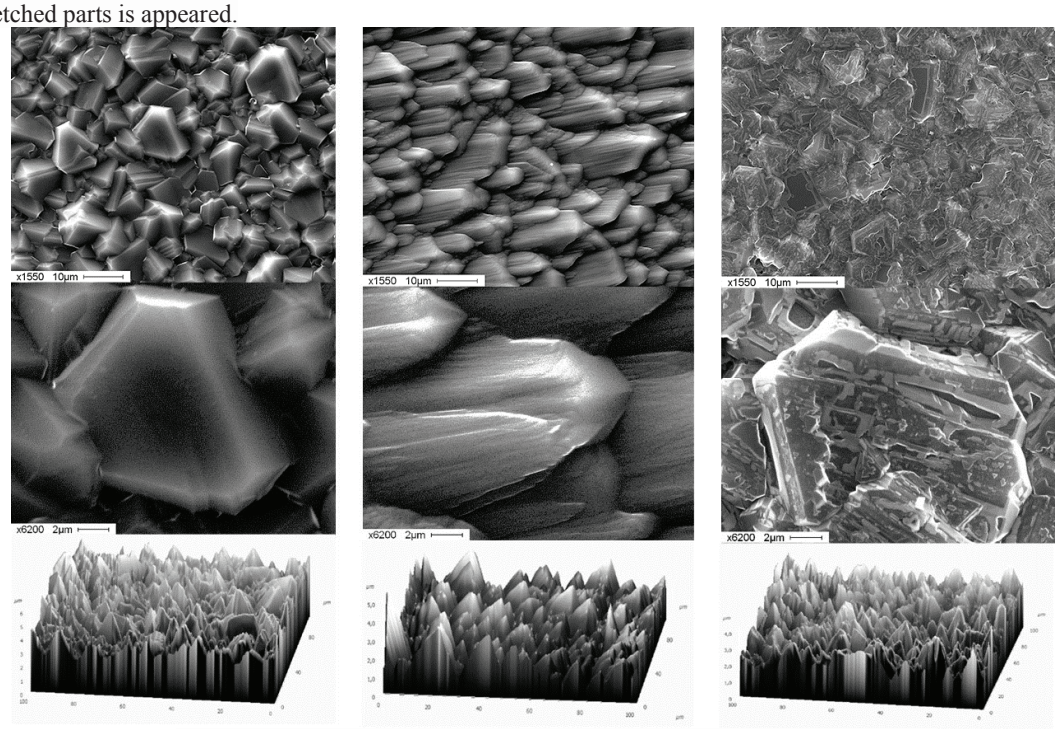
TABLE 1. Parameters of etching processes

Technology	Pressure (Torr)	Gas	Power (W)	Temperature of substrate (C°)
Ion beam etching	10^{-3}	Ar	300	25-50
Etching in a glow discharge plasma	40	H_2	5500	800±25

To vary the morphology of the surface, we used the methods of ion beam etching in the atmosphere of argon and in hydrogen plasma. The technology of ion etching is as follows: argon was injected into the chamber under a pressure of about 10^{-3} Torr and the charge was ignited [9]. The ions are "extended" under the accelerating voltage of 3.5 keV and directed onto the sample. The focused ion beam does not essentially disperse in the space [10]. Owing to this method, the surface of the diamond film is etched; the most prominent regions and peaks subject to the maximum etching [11]. The parameters of the process are shown in Table 1. Also to reduce the changes in the morphology of the surface, we used the hydrogen etching in a glow discharge plasma, the etching technology is similar to the above-described deposition process, the parameters of etching are shown in Table 1. Both etching technologies enable to carry out treatment in a wide range of sizes of the samples and regardless of their curvature [12]. The efficiency and applicability of methods were analyzed by studying the influence of treatment on the surface.

RESULTS AND DISCUSSION

The morphology of the obtained samples was studied using the scanning electron microscope (SEM-515 Philips), optical microscope (CARL ZEISS Axio Imager A2M), and atomic-force microscope (NTEGRA PRIMA NT-MDT). As Fig. 2a show, the film has a many crystal grains of different shapes and sizes with chaotically located faces. After ion etching treatment, the oriented surface is formed [12], as shown in Fig. 2b. As etching was made at an angle, the obtained structure is seen in the flat; the residual ion tracks and their profile are also seen. A high efficiency of etching and the film stability are registered; a lot of crystals form a single surface groups without destruction and flaking. Fig. 2c demonstrates the effect on the etching film in hydrogen plasma. By the AFM microscopy investigation the surface became more developed. In various points the value of surface irregularities increased by 20±5%, also this surface lost crystallinity and the many hollows and etched parts is appeared.



(a) (b) (c)

FIGURE 2. Surface morphology: a) unetched sample b) ion beam etching c) etching in hydrogen plasma.

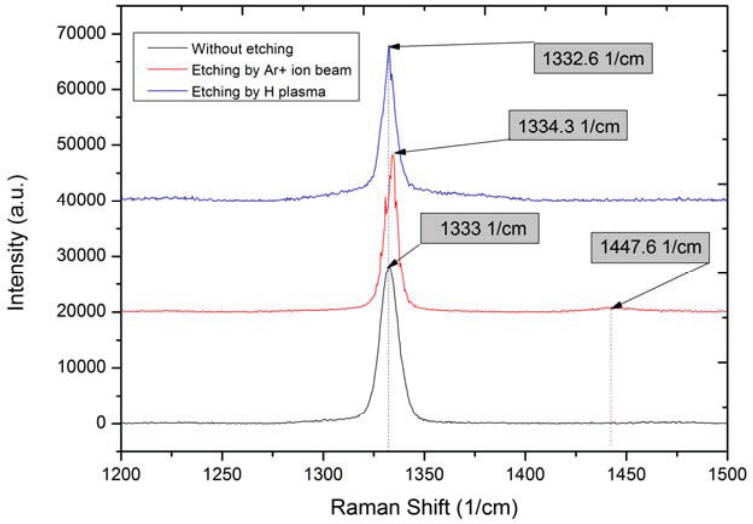


FIGURE 3. Raman spectrum of deposited diamond films.

To estimate the phase changes at different types of etching precisely, the phase composition and the purity of the synthesized diamond films were defined using the most well-known method that is Raman spectroscopy (NanoScan Technology Centaur I HR spectrometer) [11]. The spectrum given in Fig. 3 is typical for the monocrystalline diamond. The width of the line, which characterizes sp^3-carbon (1333 cm^{-1}) does not exceed 50 $см^{-1}$ that indicates the absence of the amorphous sp^3-carbon. Here the spectrum which shows the results of the ion etching reveals the line of the parasitic inclusion characteristic for the polycrystalline diamond (the trans-PA lines (1450 cm^{-1}) [13] that is the sp^2-carbon atomic chain with single hydrogen bonds for each carbon atom. The presence of such deviation is determined by the action of the ion bombardment, surface amorphization, as well as the occurrence of intergranular phases. The low intensity of the luminescence proves a low contribution of such deviations into the general composition of the film. Such peak is lacking on the samples subjected to etching in hydrogen plasma, as the hydrogen etch rate of such inclusions is much higher than that of the pure diamond. Because of this, the deposited films consist of the high-quality diamond compared to the pure monocrystalline diamond.

CONCLUSION

We obtained the high-quality coating diamond films on the hard alloy VK-8 samples using the deposition method in glow discharge plasma. Changes of their morphology during the process of etching treatment were analyzed. The ion etching in the atmosphere of argon showed a high efficiency and uniformity of the created surfaces oriented in the space. The crystallites direction repeats the angle of the ion source. Such coatings do not lose their diamond properties and becomes more uniform in the plane. Also the weak appearance of sp^2-bound transpolyacetylene phases in the composition of the film is due to the insignificant surface amorphization under ion bombardment. Such technology can be applied for thinner treatment of diamond surfaces with minimum destruction effect. The treatment in a glow discharge plasma in the atmosphere of hydrogen on the contrary creates more developed (about 20±5% from original) and nonuniform surface by the crystals destructing in the least stable locations and etching all kinds of nondiamond inclusions.

ACKNOWLEDGMENTS

This work was supported financially by the Russian Foundation for Basic Research (research project # 16-32-60018 Mol_a_dk, research project No 16-32-00008 Mol_a), Russian President's grant # MK-5516.2016.8, the Foundation for Assistance to Small Innovative Enterprises (research project # 0015685 “UMNIK 15-6”) and the Megaproject of Tomsk Polytechnic University “Materials for extreme conditions”.

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